

New Aldehyde Tanning
Studies In The United States

1408

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Introduction

The tanning action of certain aldehydes, and particularly formaldehyde, has been known for some time. I am limiting this paper to a discussion of recent research carried out the last 3 or 4 years in the U. S. A. at our Laboratory and at the Army Quartermaster Research and Development Laboratory. These researches have made significant contributions to our knowledge of aldehyde tanning, particularly in the realm of dialdehydes.

New Aldehyde Tannages

In contrast to the saturated monoaldehydes, which show a rapid decrease in tanning power with increase in molecular weight, the polyfunctional aldehydes appear to maintain tanning power with increase in molecular weight. Table I sum-

Table 1

TANNING POWER OF ALDEHYDES

ALDEHYDE	MAX. T _s , °C.		FIXED ALDEHYDE % HIDE SUBST.	% SHRINKAGE
	ACID pH	BASIC pH		
FORMALDEHYDE	87	88	1.4-2.2	
GLYOXAL	69	84	3.2-3.7	
MALONALDEHYDE	78	61	2.5-4.4	
SUCCINALDEHYDE	76(80)	70(75)	2.2-3.7	
GLUTARALDEHYDE	83	85	6.9	
3-METHYLGUTARALDEHYDE	81	82	-	
2,4-DIMETHYL-2-METHOXY- METHYLGUTARALDEHYDE	70	78	-	
α-HYDROXYADIPALDEHYDE	69	73	-	
DIALDEHYDE STARCH	76	83	6.5	

marizes the tanning power of these new aldehyde materials. For purposes of comparison, formaldehyde and glyoxal are included. The former tans over a wide pH range, whereas the latter only in the alkaline range. Malonaldehyde and succinaldehyde tan best in the acid range, pH of 3.5 to 4.5, and give shrinkage temperatures of about 78°C. ^{1,2} Succin-

aldehyde, however, was superior to malonaldehyde under all conditions tried. The next higher homologue, glutaraldehyde, turned out to be an exceptionally good tanning agent over a very wide range of pH, giving shrinkage temperatures above 82°C. ^{1,3} The tanning power of 3-methylglutaraldehyde was almost equal to that of glutaraldehyde³. These two aldehydes were the most reactive among the dialdehydes and were comparable to formaldehyde in tanning power. 2, 4-Dimethyl-2-methoxymethylglutaraldehyde, a trisubstituted glutaraldehyde, on the other hand, tanned best in alkaline solution³. Dialdehyde starch, a unique polyaldehyde derived from starch, showed better tanning properties in alkaline solution; however, in acid solution it approached succinaldehyde in reactivity ^{3,4,5}. α-Hydroxyadipaldehyde showed poor tanning properties. ^{1,3}

Also indicated in Table I is fixation of aldehyde. These values were determined by difference except for formaldehyde, which can be determined directly. The fixed aldehyde, as expected, increased with increasing molecular weight of the aldehyde. However, the three and four carbon dialdehydes seem to deviate from this generalization.

Formaldehyde and dimethyl methoxymethylglutaraldehyde produced white leathers, whereas all the other aldehydes produced cream to tan colored leathers. These colors are unstable to sunlight, which usually shows a bleaching action. Succinalde-

hyde leather is distinguished by a canary yellow color and a smooth grain. In roundness and fullness it was stated to be superior to any other aldehyde leather including formaldehyde and glyoxal¹. In our experience, however, glutaraldehyde stands out as perhaps the most valuable aldehyde tanning agent.

Tanning with Dialdehyde Starch

I would like to discuss in some detail our research on tanning with an unusual aldehyde known as "dialdehyde starch." This complex aldehyde is derived from starch by periodate oxidation as shown in Fig. 1.

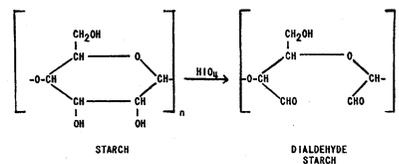


Figure 1

Periodate Oxidation of starch to Dialdehyde Starch

In this oxidation, glucose units in starch are converted to a dialdehyde structure and the process can be readily controlled to convert any desired proportion of glucose units to this structure. Our interest in this derivative was stimulated by the development in the U. S. of an efficient electrolytic process for effecting the periodate oxidation⁶. In this new process the expensive reagent, sodium periodate, is constantly regenerated electrolytically during the reaction. Thus dialdehyde starch is potentially available from a low cost, noncritical agricultural raw material. As a matter of fact, two companies in the U. S., namely Abbott Laboratories and Miles Chemical Company,* have

†Eastern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

* The mention of trade names or companies throughout this paper does not constitute an endorsement by the Department of Agriculture over other products of a similar nature not mentioned.

recently announced its commercial availability.

Dialdehyde starch is not soluble in water. However, aqueous solutions which show tanning properties may be readily prepared either by autoclaving an aqueous suspension at 120°C. for 1/2 hour or by the action of dilute alkalies, such as sodium bicarbonate or borax. Comparable tanning results were obtained by either method of solution. The latter procedure is attractive from a practical standpoint since the solid dialdehyde starch can be added to the tannage which is best carried out in an alkaline liquor. The solid dissolves gradually in the alkaline liquor, providing a gradual increase in aldehyde concentration in the tanning solution. This property facilitates production of smooth-grained leather.

We also studied the tanning action of dialdehyde starches of various oxidation levels. There was a gradual loss in tanning power as the dialdehyde content of the starch decreased. In general, maximum shrinkage temperature and the most favorable leather characteristics resulted from the dialdehyde starch of high aldehyde content. Our studies indicate that an oxidation level of about 90% or higher is desirable as regards the tanning properties of this material. Fig. 2 shows the rate of increase in the shrinkage temperature in tanning with autoclaved dialdehyde starch of 95% oxidation level. In common with other aldehydes, the maximum shrinkage temperature and its rate of attainment increased with increasing pH. In the neighborhood of pH 10 a shrinkage temperature of about 85°C. was reached in 6 hours. At pH 5 approximately 24 hours were needed to reach a shrinkage temperature of 75°C.

The fixation of dialdehyde starch in comparison with the simplest dial-

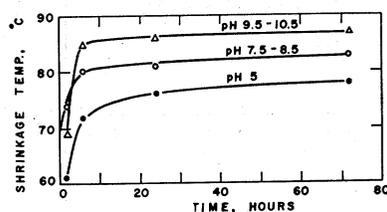


Figure 2
Rate of increase in T_s for Dialdehyde Starch Tannage

dehyde, glyoxal, was of interest in this study. The results are summarized in Table II. The data show a decrease in fixed aldehyde as the dialdehyde content or oxidation level of the starch becomes lower. The shrinkage temperature, incidentally, also follows this trend. Determination of the free amino nitrogen content also showed lower substitution of this group as the extent of oxidation became lower. Fixation of dialdehyde starch was greater at pH 7 than at pH 10, in contrast to glyoxal or formaldehyde. At pH 7 fixation of dialdehyde starch was considerably higher than fixation of glyoxal. The maximum fixation noted was 8.3% using fully oxidized starch at a pH of 7.0. Fixation was not as high as would be expected from a derivative of such a high molecular weight substance as starch. It appears probable that depolymerization of the molecule is a complicating factor in this reaction.

A study was made of the effect of four tanning factors, i.e. degree of oxidation, pH of tannage, method of solution, and fat-liquoring on the physical properties of calfskin tanned with dialdehyde starch. Table III summarizes this data. The weight yield was independent of tanning factor except, of course, for oiling. The best area yield resulted when tanning was carried out with dialdehyde starch of an intermediate oxidation level, i. e. 67%. The thickness yield and grade of leather improved

with increasing oxidation or dialdehyde content of the starch. The last column shows that each of these tanning factors had an effect on the flexibility of the leather. The flexibility improved markedly as the oxidation level of the starch increased. Tannage at pH 10 also produced a leather considerably more flexible than tannage at pH 8. Oiling, as expected, also improved flexibility greatly.

We have tanned full skins in a laboratory drum by the procedure in Table IV. Based on the drained

Table 4
Drum Tannage with Dialdehyde Starch

CALFSKIN, PICKLED	100%
WATER	200%
Na_2SO_4	26%
NaHCO_3	3.2%
DRUM 1 HR., pH 7.4	
NaHCO_3	4.3%
DIALDEHYDE STARCH, DRY	10%
DRUM 7 HRS., REST OVERNIGHT	
DRUM 2 HRS., pH 8.3	
ACETIC ACID IN 4 FEEDS	4.4%
DRUM 1 HR. AFTER EACH FEED, pH 4.6, T_s 79°C.	

pickled weight, the skin was depickled by drumming one hour in 200% water, 26% sodium sulfate and 3.2% sodium bicarbonate. An additional 4.3% sodium bicarbonate and 10% solid dialdehyde starch was added and drumming continued for 7 hours. After resting overnight the drum was run for 2 more hours. The leather was then acidified with acetic or formic acid to a pH of about 4.5 and washed. An off-white leather with a shrinkage temperature of 79°C. was obtained.

In tanning at a pH of 9 to 10, the procedure was identical except that magnesium oxide (2.5%) was used in addition to the second feed of sodium bicarbonate. At this higher pH a tan colored leather was obtained with a shrinkage temperature of 82°C. In a drum tannage, addition of the solid dialdehyde starch in feeds may be desirable in order to avoid drawn grain.

Table 2
FIXATION OF DIALDEHYDE STARCH ADDED DRY OR AUTOCLAVED

TANNAGE	FIXED ALDEHYDE, % (M.F.B.)				FREE NH_2 -NITROGEN* %
	pH 6.9-7.1		pH 9.5-10.1		
	AUTO	DRY	AUTO	DRY	
1. DIALD. STARCH, 95%	8.0	8.3	5.9	4.5	0.138
2. DIALD. STARCH, 60%	5.9	7.1	4.7	5.6	0.205
3. DIALD. STARCH, 44%	4.6	--	2.6	3.0	0.278
4. GLYOXAL	0.5		1.7		0.201

*SKIN TANNED WITH AUTOCLAVED DIALDEHYDE STARCH AT pH 7. FREE AMINO N OF UNTANNED SKIN WAS 0.473%.

Table 3
AVERAGE YIELDS, GRADE AND STIFFNESS OF DIALDEHYDE STARCH-TANNED CALFSKIN

TANNING VARIABLE	WEIGHT YIELD %	AREA YIELD %	THICKNESS YIELD %	GRADE	STIFFNESS
					Eg./cm. ²
OXID. OF STARCH, 33%	116	95	83	2.5	1737
OXID. OF STARCH, 67%	117	97	89	3.2	933
OXID. OF STARCH, 96%	115	92	99	4.4	660
STARCH AUTOCLAVED	116	94	90	3.2	1188
STARCH ADDED DRY	116	96	91	3.5	1032
TANNED AT pH 8	116	93	90	2.7	1553
TANNED AT pH 10	115	96	91	4.0	667
NOT OILED	111	93	88	2.9	1731
OILED	120	97	93	3.8	489

Tanning with Glutaraldehyde

I would like to discuss in some detail recent results that we have obtained with glutaraldehyde⁷. This five carbon dialdehyde has recently become available commercially as a 25% aqueous solution. Because of its reactivity, we felt it important to study its tanning action from a quantitative standpoint and to evaluate the leather produced.

Rate Studies:—One property of importance is the rate of tanning under various conditions. This was determined by measuring the consumption of aldehyde from the tanning liquor as a function of time. For this study an entire skin was chosen, instead of hide powder or small pieces, in order to more nearly approach tannery practice and to average out variability over the skin. This approach enabled a preliminary evaluation of the process and the properties of the leather as well.

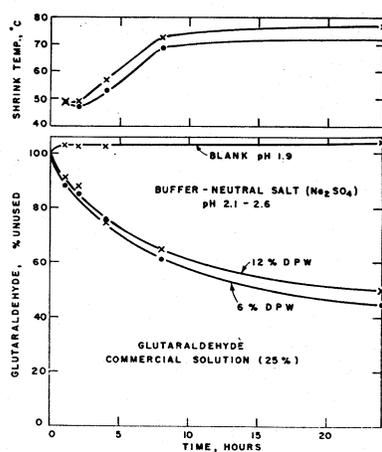
The experimental procedure was briefly as follows: A pickled degreased Syrian sheepskin was immersed in 100% water, 6% sodium chloride or 10% sodium sulfate (depending on pH under study), and glutaraldehyde which varied over 3 concentration levels. This was drummed for 1/2 hour to equilibrate the aqueous phase. The tanning liquor and a portion of the skin in the neck area were sampled to determine initial concentration of aldehyde and shrinkage temperature. Solid buffering agent was then added and drumming continued. Sampling as above was done at 1, 2, 4, 8, and 24 hours. The aldehyde content was determined by the iodimetric method.

At the same time a blank was run in order to determine whether aldehyde was consumed by side reactions brought about by pH alone. The blanks showed glutaraldehyde was stable at all pH values except at pH in the neighborhood of 9.5.

The data were plotted as % unused aldehyde against time, and the slope of the curve is a measure of the overall rate of tanning.

Fig. 3 shows the results obtained at pH of 2. to 2.5. This is the pH attained from the acidity of the pickled stock itself. The lower portion of the Figure shows aldehyde consumption and the upper portion shows rate of change in shrinkage temperature. Each curve represents a

Figure 3
Tanning rate with Glutaraldehyde at pH 2.1—2.6



different level of glutaraldehyde concentration expressed as percent of the aqueous glutaraldehyde solution, based on drained pickled weight. There is a gradual fixation of aldehyde and the shrinkage temperature increases slowly. About half of the glutaraldehyde was consumed in 24 hours and the shrinkage temperature was 72°C. or higher. You will note that fixation at this pH was slow enough so that we are reasonably accurate in assuming the aldehyde concentration, after 1/2 hour of equilibration, is substantially the initial concentration. I might point out that formaldehyde under these conditions showed no evidence of fixation or tanning. This latter agrees substantially with results of previous investigators^{8,9} who report little or no fixation of formaldehyde under these conditions, i.e. concentration of formaldehyde about 1%, pH in the range of 1-2, reaction time, 24 hours

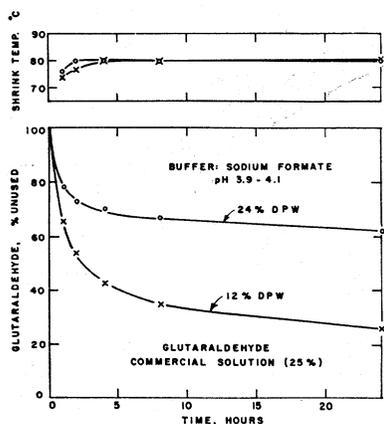


Figure 4
Tanning rate for Glutaraldehyde at pH 4.0

at room temperature.

Fig. 4 summarizes the results at pH of about 4. The rate of tanning is considerably higher than at pH 2 as shown by the greater slope of the aldehyde fixation curves and the more rapid rate of increase in shrinkage temperature. Maximum Ts was reached within 4 hours. The curves obtained at pH of 5 (Fig. 5) were

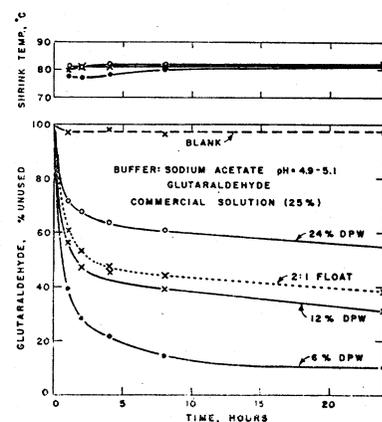


Figure 5
Tanning rate with Glutaraldehyde at pH 5.0

very similar to those at pH 4. In this case the shrinkage temperature is very nearly maximum after the first hour of tanning for the two highest levels of glutaraldehyde concentration. It is interesting to note that at a 2:1 float the rate of tanning was not markedly altered. The blank or control shows that there is no consumption of glutaraldehyde because of side reactions.

Fig. 6 shows data obtained at pH

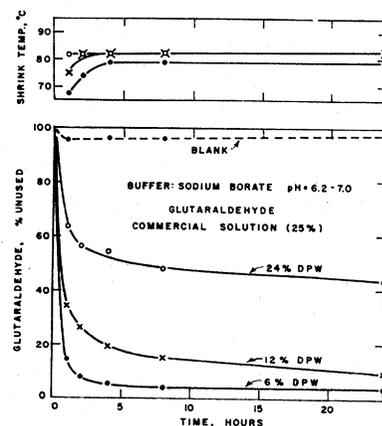


Figure 6
Tanning rate with Glutaraldehyde at pH 6.2—7.0

in the range of 6.5 to 7.0. Here we are beginning to note that consump-

tion of aldehyde is approaching 100% at the level of 6% glutaraldehyde concentration. In this case, however, the shrinkage temperature did not increase as rapidly as at pH 5.

At pH of 8, Fig. 7, both at the 6% and 12% levels the aldehyde was virtually completely consumed. The

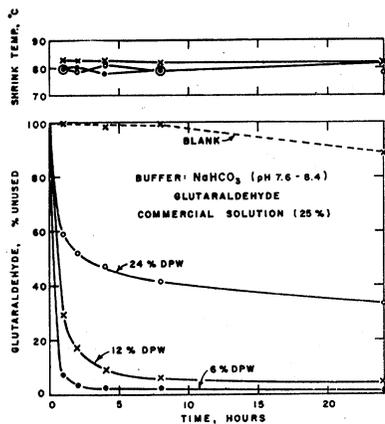


Figure 7

Tanning rate with Glutaraldehyde at pH 7.6-8.4

slope of the curves show the very rapid rate of tanning. Similarly the shrinkage temperature also illustrates this same conclusion, maximum T_s being reached in one hour. That the glutaraldehyde is stable at this pH is shown by the blank.

At pH of 9.5, Fig. 8, the picture

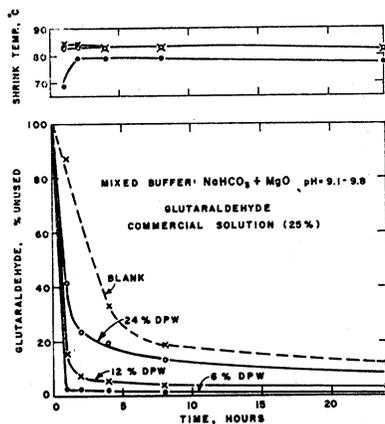


Figure 8

Tanning rate with Glutaraldehyde at pH 9.1-9.5

is complicated by the instability of glutaraldehyde. As shown by the blank, glutaraldehyde rapidly disappears due to pH effects alone. Half of the glutaraldehyde disappears in 2.5 hours at this high pH. However, the rate of tanning is more rapid and tanning takes preference even in this region of instability. At the lower

glutaraldehyde feeds, equilibrium was reached in about 2 hours with consumption of 95% or more of aldehyde.

Figure 9, is a composite of data shown previously for the 12% level

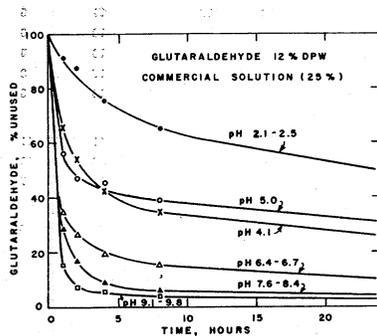


Figure 9

Rate of tanning with Glutaraldehyde at various pH levels

of glutaraldehyde and more clearly shows the rate of tanning at various pH conditions. It is evident that the rate of tanning increases with pH. Equally important this rate can be controlled between wide limits. The exhaustion of glutaraldehyde also increases with pH and in the alkaline region was essentially complete.

A comparison of the tanning properties of glutaraldehyde, glyoxal, and formaldehyde at pH 5 is shown in Figure 10. These three aldehydes

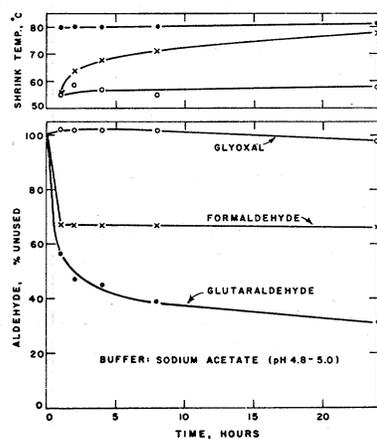


Figure 10

The rate of tanning of various aldehydes at pH 5

were employed under the same conditions which were equivalent to the tanning procedure using 12% glutaraldehyde. The glyoxal was a purified grade, free of formaldehyde and ethylene glycol, impurities occurring in the commercial product. At pH 5 glyoxal showed no tanning properties, in accordance with Gustavson's observations⁸. Formaldehyde rapidly reached a state of equilibrium with

regard to concentration of aldehyde in the tanning liquor but the shrinkage temperature showed a steady rise. Glutaraldehyde rapidly attained maximum shrinkage temperature, however, fixation of aldehyde continued in a gradual manner.

Figure 11 shows a comparison

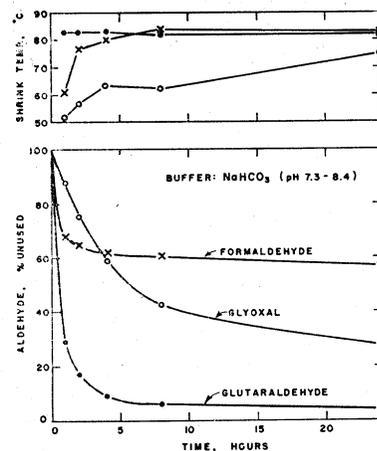


Figure 11

The rate of tanning of various aldehydes at pH about 8

among these three aldehydes at pH 8. We note a gradual fixation of glyoxal with a slow rise in shrinkage temperature. Formaldehyde and glutaraldehyde show a more rapid rate of tanning. In the formaldehyde tannage, shrinkage temperature increased more rapidly than the glyoxal but less rapidly than the glutaraldehyde tannage. We also note virtually complete exhaustion of glutaraldehyde whereas formaldehyde is far from exhausted. The same order of reactivity is noted: glyoxal is less active than formaldehyde, which, in turn, is less active than glutaraldehyde. The differences in reactivity, however, are not as pronounced as at pH 5.

Properties of the Leather:—The skins obtained at the end of 24 hours from the above rate study were processed with regular packs in a tannery into finished garment leather. No difficulty was experienced with the glutaraldehyde leather in the conventional post tanning processes. All of the leathers were judged to be soft and mellow and of pleasing leather character. Suitable leather was obtained over the entire pH range of 2 to 10 and with as little as 6% glutaraldehyde solution, which is actually only 1.5% of pure aldehyde¹⁰.

An unexpected property of the glutaraldehyde-tanned leather was its perspiration resistance as measured by area change caused by a synthetic

perspiration test proposed by Colin-Russ. Figure 12 summarizes the

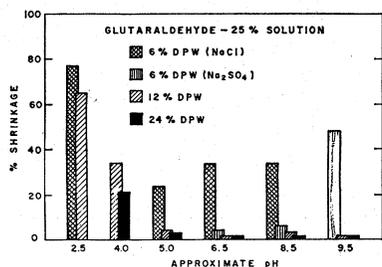


Figure 12
Influence of tanning factors on perspiration resistance of Glutaraldehyde leathers

results of this test on leathers produced under various conditions. Tannage with glutaraldehyde at the 12% level at pH 5 and above produced leather which showed unusually good resistance to this test, as indicated by a low area shrinkage, 1-6%. This tannage carried out at pH 4 and below did not result in perspiration resistant leather. With one exception, perspiration resistance was not a noteworthy property of the leathers tanned with 6% glutaraldehyde. This exception was noted when sodium sulfate was used instead of sodium chloride in the tannages carried out at pH 6.5 and 8.

A comparison of the perspiration resistance of glutaraldehyde leather with that from formaldehyde and glyoxal is shown in Figure 13. These

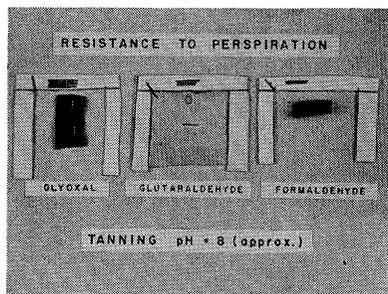


Figure 13

are specimens photographed after the perspiration test. Obviously glutaraldehyde gave a decidedly superior result in this test. Of course, I should emphasize that all three tannages were carried out under the same conditions.

The resistance of the glutaraldehyde tannage to soap solution also was investigated to evaluate this tannage from a washability standpoint. The standard AATCC Method was employed. In this instance the change in Ts of the leather as well as appearance of the specimens after testing were used as criteria of stability.

Table V. summarizes the results. In

Table 5

EFFECT OF WASHING ON Ts

TANNAGE	pH	Ts, °C.		ΔTs °C.
		INITIAL	AFTER 3rd WASH	
GLUTARALDEHYDE				
12	4.1	77	71	6
12	5.0	76	70	6
12	6.7	77	73	4
12	8.4	79	77	2
12	9.6	79	74	5
FORMALDEHYDE				
4.9	4.8	72	61	11
4.9	8.0	79	66	13
4.9	9.9	78	71	7
GLYOXAL				
5.8	8.1	73	67	6

general, the change in Ts was least for the glutaraldehyde specimens. Only in the case of glutaraldehyde was a Ts as high as 77°C. noted after the third wash. In the tannages carried out at lower pH, glutaraldehyde leathers were distinctly more resistant to lowering of the Ts by this test. All of the washed leathers were firmer after drying than the unwashed samples. However, a slight mechanical action readily restored the soft and flexible character to the glutaraldehyde leathers.

The data presented were obtained for 24-hour tannages with the laboratory drum turning intermittently overnight. We realize that this is not practical for drum tanning. It was found that with the drum at rest overnight, streaks developed in the leather. The rate curves you have seen show that tanning can be accomplished in much less than 24 hours. If tanning is carried out too rapidly, drawn grain results. With proper control, such as feed or pH control, this can be avoided. With regard to pH control, we have noted that a pH of approximately 4.2 was critical when all the glutaraldehyde at the 12% level was in one feed. Table VI summarizes a procedure found

Table 6
8 Hour Drum Tannage with Glutaraldehyde

PICKLED SKIN	100%
WATER	100%
NaCl	6%
GLUTARALDEHYDE (25% Soln.)	12%
Drum 1/2 hr., pH 2.3	
Add: NaHCO ₃	4%
Drum 2 hrs., pH 4.0, Ts 79°C.	
Add: NaHCO ₃	3%
Drum 1-1/2 hrs., pH 6.6	
Add: NaHCO ₃	1/2%
Drum 2 hrs., pH 7, Ts 82°C.	
Add: FORMIC ACID	1-3/4%
Drum 1/2 hr., pH 4.4	
Wash 1/2 hr., Ts 83°C.	

satisfactory for completion of the tannage in 8 hours.

The pickled skins were drummed for one-half hour in 100% water,

6% salt, and 12% of the aqueous (25%) glutaraldehyde solution. Sodium formate, 4%, was added and drumming continued for 2 hours. The pH and Ts at the end of this time were 4.0 and 79°C., respectively. Sodium bicarbonate, 3.5%, was added in two feeds which brought the pH to 7.0 and the Ts to 82°C. after 3½ hours additional drumming. The skins were acidified to pH of 4.4 with 1.75% formic acid and finally washed.

Sodium formate was an excellent buffer which provided almost automatic control just below the critical pH. One or two hours at this pH permitted sufficient tanning so that drawn grain was avoided upon subsequent elevation of pH.

The leathers tanned in 8 hours showed substantially the same properties as those tanned for 24 hours.

New Technique in Aldehyde Tanning

I would now like to discuss some work by Dr. Seligsberger and co-workers, who developed a new technique for tanning with aldehydes, which was particularly valuable in formaldehyde and glyoxal tanning¹. The hazards of obtaining hard, cracky leather with formaldehyde tannage are well known. The principal difficulty arises from the fact that dilute alkaline solutions cause the hide to swell just as dilute acids do. Even the use of sodium sulfate, which was shown by Kuntzel to suppress alkaline swelling, was not satisfactory since the leather was flat and tinny. A startling improvement in the character of the leather was noted when Dr. Seligsberger used fairly concentrated solutions of alkali carbonates and bicarbonates. The leather obtained had a strong grain and was full and pliable even without fat-liquoring. Glyoxal leather differs from that made with formaldehyde only by its light tan color and a shrinkage temperature of a few degrees lower. Salient features of the new tanning process are: (a) The tannage proceeds in aqueous mixtures of alkali carbonates with bicarbonates which must be strong enough to suppress swelling. A proper concentration is about 1.5 N, after reaching equilibrium with the water volume in the hide. (b) A very important step in the success of this tannage is the neutralization of the tanned hides in a fresh salt bath by the gradual addition of acid prior to

rinsing or washing. Failure to observe these two features resulted in a weaker leather and cracky grain.

Aldehyde Pretannage for Sole Leather

New knowledge concerning the tanning action of aldehydes stimulated research on the evaluation of these materials as a pretannage for a rapid process of tanning sole leather.

Seligsberger applied his new technique, discussed above, for pretanning with glyoxal, formaldehyde or mixtures of these. He prefers to use a mixture of technical solutions of glyoxal and formaldehyde in the ratio of about 7 to 1 with stock that has been delimed¹¹. Advantages of glyoxal over formaldehyde are greater ease in handling and less likelihood to cause a drawn grain. His procedure in a test on ten sides is shown in Table VII. The process

Table 7
Glyoxal Pretannage
(based on 1000 lbs. white weight)

ALKALIZING (in paddle - 70°F.)	
RATIO, SKIN TO LIQUOR	1:5
NaHCO ₃ (per 100 gals.)	42 lbs.
Na ₂ CO ₃ (per 100 gals.)	52 lbs.
RUN INTERMITTENTLY 8 HRS.; REST OVERNIGHT	
TANNAGE (in drum - 70°F.)	
VOLUME OF ALKALIZING LIQUOR	80 gals.
pH	9.5
GLYOXAL (30%) IN 4 FEEDS	70 lbs. (7%)
FORMALDEHYDE (36%) IN LAST FEED	10 lbs. (1%)
RUN INTERMITTENTLY 5 HRS.; REST OVERNIGHT	
ACIDIFY TO pH 3.8 (drum)	

comprises four stages. The first equilibrates the hide with a nonswelling, alkalizing liquor (1.5 N in carbonate plus bicarbonate). A paddle was used because of scarcity of drums in a sole leather tannery. Economy of chemicals can be effected by carrying out this stage in a drum. However, laboratory experiments show that a portion of the alkalizing liquor can be reused in the paddle operation.

In the second stage the tannage is carried out in a drum, using 7% glyoxal and 1% formalin (based on the stock) at a pH of 9.5. Maintaining a temperature of less than 85°F. in the tan drums is essential for the success of this tannage.

The third stage comprises lowering the pH to 3.8 after the tannage and was also carried out in a drum. To effect economy of acid, 1/3 of the

tanning liquor was discarded before acidification.

The fourth stage, Table VIII, was the retannage. In some tests this was effected with liginosulfonate at pH of 2.0 to 2.5 in rockers over a five-day period. The liginosulfonate used was the sodium salt of hardwood liginosulfonate. In one test the retannage was effected with a blend of 70% vegetable extract (sulfited quebracho) and 30% liginosulfonate. In this instance the retannage was

Table 8
Retannage of Glyoxal
Pretanned leather with
Liginosulphonate

1st ROCKER - 1 DAY	
BARKOMETER	45°
TEMPERATURE	120°F.
pH	2.6
2nd ROCKER - 1 DAY	
BARKOMETER	60
TEMPERATURE	120°F.
pH	2.2
3rd ROCKER - 3 'A'	
TEMP., 120 F. FALLING TO ROOM TEMP.	
BARKOMETER, LIQUOR FROM 2nd ROCKER, NOT STRENGTHENED.	

carried out at pH 3.9 over the same number of days. This process speeds up the sole leather tannage so that no more than 7-8 days are required from the dehairing to the bleaching operations. All the subsequent operations were those conventionally used in sole leather processing.

Table IX shows some properties of

Table 9
Analysis of Glyoxal
Pretanned Sole Leather

PROPERTY	RETANNAGE	
	100% LIGNO-SULFONATE	70% VEGETABLE 30% LIGNO-SULFONATE
HIDE SUBSTANCE, %	50.1	44.4
COMBINED TANNIN, %	25.0	28.5
DEGREE OF TANNAGE	50.0	64.2
T _s , °C.	81	82
COMPRESSIBILITY, %	10.9	9.5
DENSITY	0.94	0.97
THICKNESS (IRONS)	9.6	10.1
WATER ABSORPTION, %	45.9	41.3

glyoxal pretanned finished sole leather. Most of the figures for chemical and physical data conform to accepted standards for sole leather. A notable exception is the low degree of tannage for the leather produced by retannage with liginosulfonate alone. When the blend containing only 30% liginosulfonate was used, the degree of tannage rose a

full 14 units, accompanied by a marked increase in thickness and density. Another difference between retannage with liginosulfonate alone and with the blend is the higher water absorption of the former. In comparison to the conventional tannages the water absorption is high. Oil treatment, required for military sole leather, lowered the water absorption to about 15%. Conspicuous is the marked lowering of shrinkage temperature when retannage was carried out with liginosulfonate alone.

Probably the most remarkable property of this finished leather was its flexibility, which is comparable to the flexible type sole leather currently in demand. Color and appearance of the grain were rated good by experienced tanners.

Because of its availability from agricultural raw materials, our laboratory was naturally interested in evaluating dialdehyde starch as a pretannage for sole leather. A series of 21 tests on a scale of one side per test was run to evaluate various tanning variables¹². Each side, after delimiting, was pretanned by immersion in an 8% sodium sulfate solution containing the solid dialdehyde starch. The pH of the solution was adjusted between 7.8 and 8.4 with sodium bicarbonate. In a drum tannage penetration of the dialdehyde starch was complete after 7 hours of intermittent drumming. In a still vat the pretannage required only 24 to 48 hours. Although more rapid, the drum tannage often caused a drawn grain in these tests. The shrinkage temperature of the dialdehyde starch pretanned hides ranged from 75-80°C.

Retannage was effected at pH 4.0 in a liquor containing 15% tannin comprising 50% sulfited quebracho and 50% chestnut. In a drum, retannage penetration was complete after 8 hours drumming and an overnight rest period. In a still vat penetration was complete in 4 to 5 days. Drum tanning was more rapid than vat tanning during the vegetable retannage with little danger of drawn grain except for a moderate amount in hides pretanned with only 5% dialdehyde starch. Retannage raised the shrinkage temperature of the finished leather to about 85°C. The leathers were finished at a commercial tannery by the usual methods.

In this series of tests the vegetable tanning liquors were reused after re-

